PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-172933
(43)Date of publication of application : 21.06.1994

(51)Int.Cl. C22C 38/00
C22C 38/22
C22C 38/28

(21)Application number : 04-351238
(22)Date of filing : 07.12.1992

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(54) AL-CONTAINING FERRITIC STAINLESS STEEL EXCELLENT IN PRODUCIBILITY AND HIGH-TEMPERATURE OXIDATION RESISTANCE

(57)Abstract:
PURPOSE: To obtain Al-contg. ferritic stainless steel free from the generation of abnormal oxidation even if being heated in an oxidizing atmosphere of 1150°C for a long time and good in toughness and producibility.
CONSTITUTION: This Al-contg. ferritic stainless steel contains by weight, ≤0.03% C, ≤0.2% Si, ≤0.3% Mn, ≤0.04% P, ≤0.003% S, 15 to 25% Cr, ≤0.03% N, 1 to <4.5% Al and 0.5 to 2% Mo and furthermore as necessary, V and/or Ti by 0.01 to 0.5% in total and one or ≥ two kinds among rare earth elements and Y by 0.01 to 0.15% in total, and the balance substantial Fe. By adding Mo in the conditions of low Mn and Si, its high-temp. oxidation resistance can be improved, and because of low Al content, its toughness and producibility can also be secured.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to aluminum content ferritic stainless steel suitable for the use put to the high temperature atmosphere of an automobile exhaust device, a space heating appliance, etc.
[0002]
[Description of the Prior Art]aluminum content ferritic stainless steel showed the outstanding high-temperature-oxidation-proof characteristic, and has been widely used as heaters and the charges of electric heat material, such as vapour-chimney material of a stove. These days, it replaces with the ceramics used from the former as a substrate of the catalytic converter in the diesel-particulate filter of a car, and aluminum content ferritic stainless steel is used increasingly. In a thermal shock, weakly, since the ceramics as a conventional substrate for catalytic converters have large calorific capacity, they have defects, like carrying out temperature up to catalytic-reaction temperature takes time. In the metallic converter which uses metal, such as ferritic stainless steel containing high Al, as a substrate, the defect resulting from these ceramics is improvable.
[0003]The foil material of about 50 micrometers of board thickness is used for the substrate of a metallic converter. However, in a foil material, it is easy to generate catastrophic oxidation. Since it is used in the exhaust gas atmosphere which is severe oxidation conditions, the high-temperature-oxidation-proof characteristic of having excelled dramatically is required of a substrate. ferritic stainless steel containing high Al which added aluminum effective in an improvement of the high-temperature-oxidation-proof characteristic so much, and added a rare earth element (it is hereafter written as REM) and Y at this point attracts attention -- for example, 20Cr-5 aluminum-REM and Y system -- stainless steel is used. For example, aluminum content ferritic stainless steel which improved the high-temperature-oxidation-proof characteristic is introduced by JP,4-128344,A by adding 0.01 to 0.5% of the weight of Y. In order to improve oxidation resistance in JP,4-128345,A under the conditions which held down ingredient cost as low as possible, 0.06 to 0.15% of the weight of Ln (lanthanide group element) is added, And aluminum content ferritic stainless steel which has improved hot-working nature is introduced by making P of the quantity specified by the relation with Ln contain.
[0004]
[Problem(s) to be Solved by the Invention]Although the metallic converter is excellent in

exhaust gas purification performance as compared with the ceramic converter, its raw material cost is high and it is difficult to manufacture. That is, since the conventional ferritic stainless steel currently developed as an object for metallic converters contains a lot of Cr(s) and aluminum, toughness is not enough and there is a problem in molding workability. If REM and Y are added in order to improve the high-temperature-oxidation characteristic, the toughness of slab and a hot coil will fall remarkably. As a result, it is easy to generate a crack in the cases, such as hot-rolling, and working capacity and a manufacturing yield are low, and have become the cause of raising steel-materials cost.
[0005]Processability improves by reducing Al content. Only by reducing Al content, the high-temperature-oxidation-proof characteristic falls and it stops however, being suitable for the use as a metallic converter. Therefore, it is the actual condition of making processability into a sacrifice to some extent, and making about 5% of aluminum containing. Thus, low processability has been an obstacle when a metallic converter spreads. then, conventional 20Cr-5 aluminum-REM [in which toughness is good and it is easy to manufacture it / with low steel-materials cost], and Y system -- material in which stainless steel and the high-temperature-oxidation-proof characteristic more than equivalent are shown is desired. This invention is thought out so that it may meet such a demand, and it is a thing.
By adding a little REM and/or Y with Mo of a specific amount to aluminum content ferritic stainless steel under the conditions which reduced the purpose and Si, It is providing the ferritic stainless steel which had the high-temperature-oxidation-proof characteristic which is equal to the conventional stainless steel for metallic converters, and was excellent in manufacturability.

[0006]
[Means for Solving the Problem]aluminum content ferritic stainless steel of this invention, In order to attain the purpose, C:. 0.03 or less % of the weight, less than Si:0.2 % of the weight, less than Mn:0.3 % of the weight, P:0.04 % of the weight or less, S:0.003 % of the weight or less, Cr:15-25 % of the weight, N:0.03 % of the weight or less, aluminum : At 1 % of the weight or more, less than 4.5 % of the weight, Mo:0.5-2 % of the weight, REM. And one sort or two sorts or more of Y: Satisfy Mo%>=5x (Mn%+Si%) in total including 0.01 to 0.15 % of the weight. This aluminum content ferritic stainless steel can also contain 0.01 to 0.5 % of the weight for V and/or Ti in total further.
[0007]
[work --] for That conventional ferritic stainless steel containing high Al currently used as an object for metallic converters shows low toughness has a cause in containing a lot of Cr(s) and aluminum. Although an improvement of toughness is achieved by fall of Al content, the high-temperature-oxidation-proof characteristic deteriorates only by making Al content low. This invention persons investigated and studied influence which various alloy elements give Al content about less than 4.5% of the weight of reduced ferritic stainless steel so that good toughness may be secured. As a result, when making Mo contain under conditions which reduced Mn and Si, even if it was less than 4.5% of the weight of low Al content, it found out that the outstanding high-temperature-oxidation-proof characteristic was obtained.
[0008]Although Mo of the high-temperature-oxidation-proof characteristic of aluminum

content ferritic stainless steel is effective in an improvement, an effect of this Mo becomes remarkably large by reduction in Mn, and low Si-ization. Although the detailed reason is unknown, the high-temperature-oxidation-proof characteristic which is equal to 4.5% of the weight or more of ferritic stainless steel containing high Al can be given. And good toughness and processability are also secured from there being little Al content. This invention is completed as a result of investigating and studying influence of various alloy elements on developmental mechanics of catastrophic oxidation under this high temperature atmosphere. That is, even when adding a little REM, and/or Y and Mo under conditions which fell a Mn content and a Si content, and the high-temperature-oxidation-proof characteristic of having excelled dramatically was obtained and it held for a long time to an elevated temperature which is 1150 **, it found out that starting catastrophic oxidation was lost. Although the detailed reason of reduction in Mn and reduction in Si is unknown, they are imagined to have contributed an operation of Mo, REM, Y, etc. to making it demonstrate effectively. Therefore, it is not necessary to add a lot of Mo, REM, Y, etc., and good processability and intensity are also secured.
[0009]Hereafter, an alloy element contained in aluminum content ferritic stainless steel of this invention and its content are explained.
C: It becomes easy to generate catastrophic oxidation with an increase in C content. A lot of C content degrades the toughness of slab and a hot coil, and it becomes difficult to process it into a plate by hot working. Therefore, in this invention, a maximum of C content was specified to 0.03% of the weight.
Si: Generally, when Si improves the high-temperature-oxidation-proof nature of stainless steel, it is validated, and it is added as a positive alloy element by stainless steel for high temperature oxidation-proof. However, in aluminum content ferritic stainless steel, an improvement of high-temperature-oxidation-proof nature is achieved, and it becomes difficult to generate catastrophic oxidation by reducing Si as much as possible. An effect by such Si reduction is the phenomenon found out by this invention person etc., and shows up notably in 0.2 or less % of the weight of Si contents.
[0010]Mn: When raising hot-working nature, it is an effective alloy element, but in high aluminum ferritic stainless steel, it has an adverse effect on the high-temperature-oxidation-proof characteristic, and catastrophic oxidation occurs for a short time. Influence which a Mn content has on the high-temperature-oxidation-proof characteristic is the phenomenon which this invention person etc. found out, Mn mixes into an aluminum$_2O_3$ coat formed in a surface of this component system steel, and makes an oxide of Cr system which has an adverse effect on the high-temperature-oxidation-proof characteristic, and a Mn system generate, and promotes generating of catastrophic oxidation. Control catastrophic oxidation, and the high-temperature-oxidation-proof characteristic is raised, and also as for a Mn content [from], lessening as much as possible is preferred. Toughness also improves with a fall of a Mn content. However, since it mixes from a scrap which is a raw material for steel manufacture, falling a Mn content extremely causes a rise of a manufacturing cost. Then, in this invention, a maximum of a Mn content was preferably specified to 0.2% of the weight 0.3% of the weight.
[0011]P: It is an element which has an adverse effect on the high-temperature-oxidation-proof characteristic, and the lower one is preferred. If P content is high, the toughness of a hot-rolling board will also fall. Then, in this invention, P content was specified to 0.04

or less % of the weight.
S: Combine with REM and Y, and it becomes sulfide system inclusion, and worsen a surface disposition of steel. REM and Y which contribute to the high-temperature-oxidation-proof characteristic are consumed by generation of a sulfide. Therefore, it is necessary to add a lot of REM, Y, etc., and the toughness of steel is degraded. Evil by S will appear notably, if content exceeds 0.003 % of the weight. Then, in this invention, a maximum of S content was preferably specified to 0.002% of the weight 0.003% of the weight.
[0012]Cr: It is a fundamental alloy element required in order to improve the high-temperature-oxidation-proof characteristic of steel. By making 15% of the weight or more of Cr contain, a strong oxide film is formed and catastrophic oxidation of steel is controlled. However, if a lot of Cr(s) exceeding 25 % of the weight are contained, the toughness of slab and a hot coil will fall and manufacturability will worsen. Therefore, in this invention, a Cr content was set as 15 to 25% of the weight of a range.
N: Combine with aluminum in steel and generate AlN used as a starting point of catastrophic oxidation. The toughness of stainless steel is fallen and manufacturability is worsened. Then, in this invention, a maximum of N content was specified to 0.03% of the weight.
[0013]aluminum: It is an alloy element required in order to maintain the high-temperature-oxidation-proof characteristic like Cr, and the high-temperature-oxidation-proof characteristic of having excelled by forming aluminum$_2O_3$ in a surface is given. In order that especially board thickness may fully develop an aluminum$_2O_3$ layer effective in control of catastrophic oxidation in a foil material of 100 micrometers or less, 1% of the weight or more of aluminum is made to contain. However, if a lot of aluminum is contained to 4.5% of the weight or more, the toughness of slab and a hot coil will deteriorate and a fall of a manufacturing yield and by extension, a rise of steel-materials cost will be caused. Then, in this invention, Al content was set as less than 4.5% of the weight of a range at 1 % of the weight or more in consideration of toughness and processability.
[0014]Mo: It is an alloy element which plays an important role in stainless steel of this invention. Conventionally, since Mo tends to form a volatile high oxide, it is supposed that it is deteriorated in the high-temperature-oxidation-proof characteristic of steel. However, in reduction in Si, and stainless steel of this invention formed into low Mn, the high-temperature-oxidation-proof characteristic is remarkably improved by addition of Mo, and it becomes what was excellent also in high temperature strength. An effect of such Mo shows up notably in 0.5% of the weight or more of content. However, if Mo is made to add so much, the toughness of steel will deteriorate and manufacturability will worsen. Then, in this invention, Mo content was set as 0.5 to 2% of the weight of a range.
[0015]REM and Y : In order to improve the high-temperature-oxidation-proof characteristic of high aluminum ferritic stainless steel, it is an important alloy element. If REM, such as La and Ce, and Y are added, an oxide film formed in the steel-materials surface will elaborate, and it will become the thing excellent in stability. As a result, catastrophic oxidation which is easy to generate with a foil material is controlled. The adhesion of an oxide film to Ko Shimoji also improves.
[0016]An effect which REM and Y give to oxidation-resistant improvement and control of catastrophic oxidation becomes remarkable by 0.01% of the weight or more of content.

However, if a lot of REM and Y exceeding 0.15 % of the weight are made to contain, hot-working nature and toughness will get worse, and manufacture will become difficult. A lot of REM and Y content make a deposit of nonmetallic inclusion used as a starting point of catastrophic oxidation promote, and degrade the high-temperature-oxidation-proof characteristic on the contrary. Therefore, in this invention, content of REM and Y was set as 0.01 to 0.15% of the weight of a range in total.
[0017]V and Ti: It is an alloy element added by aluminum content ferritic stainless steel of this invention if needed, and an operation which improves the toughness of steel remarkably is presented by combining with C in steel, or N. Stainless steel used for high-temperature-service ways, such as a metallic converter, is put to environment where an oxide film exfoliates easily in order to receive a cold and hot cycle. In addition to REM and Y which were mentioned above, the adhesion of an oxide film to Ko Shimoji can improve also by V or Ti. Then, an addition of REM and Y which lead to a fall of toughness or a rise of steel-materials cost easily can be stopped low, and the part can be compensated with V or Ti. This gives dramatically outstanding adhesion to an oxide film, and it becomes possible to control catastrophic oxidation. In order to acquire such an effect, it is required to make 0.01% of the weight or more of V or Ti contain in total. However, if a lot of V or Ti are contained exceeding 0.5 % of the weight, steel will become hard and processability will deteriorate. So, in making V or Ti contain, it sets up the range to 0.01 to 0.5% of the weight.
[0018]
[Example]
Example 1: After carrying out vacuum melting of the various stainless steel shown in Table 1 and performing forge, cutting, and hot-rolling, annealing and cold rolling were repeated and the foil material of 50 micrometers of board thickness was manufactured. A 1150 ** oxidation test was presented with the obtained foil material, and time until catastrophic oxidation occurs was investigated. Generating of catastrophic oxidation took out each test specimen from the heating furnace suitably, and judged it by carrying out visual observation of the letter oxide of upheaval other than the thin and uniform oxide film usually detected. And total oxidation time until this letter oxide of upheaval is observed was shown in Table 1 as catastrophic oxidation generating time. In Table 1, the examination sign A is steel currently used from the former as an object for metallic converters.
Catastrophic oxidation is not started by a 1150 ** heating test till 170 hours.
The examination sign B is the steel which lowered Al content to 3 % of the weight as compared with A steel.
Catastrophic oxidation has occurred in 85 hours.
Catastrophic oxidation occurred in 80 hours with the steel C which lowered Al content and a Cr content to 3 % of the weight and 18 % of the weight, respectively. This shows stopping having the high-temperature-oxidation characteristic demanded as an object for metallic converters only by lowering a Cr content and Al content targeting an improvement of toughness.
[Table 1]

表1：合金成分と異常酸化発生時間及び衝撃靭性との関係

試験記号	合金成分及び含有量（重量%）									異常酸化発生時間（時）	衝撃靭性（J／cm²）	適用
	C	Si	Mn	P	S	Cr	Al	Mo	REM, Y			
A	0.012	0.35	0.34	0.024	0.0021	20.16	5.22	—	0.06	170	11	比較鋼
B	0.014	0.35	0.27	0.023	0.0021	20.19	3.14	—	0.06	85	23	
C	0.015	0.34	0.33	0.024	0.0020	18.02	3.30	—	0.07	80	36	
D	0.013	0.36	0.32	0.024	0.0019	20.09	3.41	0.51	0.04	190	29	
E	0.012	0.34	0.31	0.022	0.0018	20.16	3.37	1.03	0.04	220	21	
F	0.011	0.34	0.34	0.024	0.0020	20.01	3.31	1.52	0.05	250	16	
G	0.012	0.33	0.35	0.021	0.0021	20.29	3.26	1.91	0.06	270	13	
H	0.013	0.34	0.12	0.024	0.0020	20.05	3.29	1.88	0.06	300	17	
I	0.012	0.35	0.11	0.025	0.0019	20.08	3.43	1.79	0.06	310	21	
J	0.011	0.18	0.08	0.024	0.0019	19.15	3.36	1.83	0.04	320	26	本発明鋼
K	0.013	0.12	0.10	0.024	0.0021	20.14	3.35	1.85	0.05	350	28	
L	0.013	0.10	0.08	0.022	0.0020	20.10	3.32	1.93	0.05	370	31	

[0019]In the range which is 3 to 4 % of the weight of Al content from which good toughness is secured, other alloy elements investigated the influence which it has on the high-temperature-oxidation-proof characteristic. They reduce toughness remarkably as REM, Y, etc. by which it is known that it is effective in an improvement of the high-temperature-oxidation-proof characteristic have a very high raw material price and their addition moreover increases. Therefore, in this example, examination was advanced within the limit of 0.06 % of the weight of additions of REM and Y. In process of this examination, it found out that the high-temperature-oxidation-proof characteristic was

improved by Mo addition. Examination sign D-G of Table 1 is the steel which investigated the influence of Mo content given to the high-temperature-oxidation-proof characteristic. When the test result about the high-temperature-oxidation-proof characteristic of D-G steel is arranged by a relation with Mo content, as shown in drawing 1, the high-temperature-oxidation-proof characteristic is improved with the increase in Mo content, and time until catastrophic oxidation occurs is long.However, as for the hot coil which has hot-rolled D-G steel, the tendency for toughness to fall with the increase in Mo content is seen.

[0020]Recovery of toughness was seen, when Mo was added under the conditions which fell the Mn content so that it may be shown as the examination signs H and I. The fall of the Mn content was effective also in the improvement of the high-temperature-oxidation-proof characteristic. Although quantitative formulas other than Mn of H steel and I steel are almost the same as that of G steel, their toughness is improving as compared with G steel.

Time until it generates catastrophic oxidation is also long.

However, when taking into consideration manufacture by a mass production line, controlling low the content of Mn mixed from a scrap investigated the influence which other alloy elements have from the difficult thing. As a result, when reducing Si with Mn, it turned out that toughness and the high-temperature-oxidation-proof characteristic are improved further.

[0021]From the former, Si is used as an element effective in an improvement of the high-temperature-oxidation-proof characteristic of stainless steel, and is added positively. However, when based on this invention person's etc. examination, in aluminum content ferritic stainless steel which added Mo, the high-temperature-oxidation-proof characteristic deteriorated on the contrary with the increase in a Si content, and it became clear that it became easy to generate catastrophic oxidation. For example, the high-temperature-oxidation-proof characteristic of the Si content having become low so that the Mo addition aluminum content ferritic stainless steel (examination sign J-L) to which the Si content was reduced might see, and having excelled is shown. The toughness of J-L steel with few Si contents shows the remarkable big value as compared with G steel.

[0022]In order that Si may acquire the deoxidation effect, it may be added, but there is no necessity in particular for Si deoxidation from having added big aluminum of the deoxidation effect so much in aluminum content ferritic stainless steel. Therefore, it is possible to face to manufacture with a mass production line and to make a Si content low as much as possible. When adding Mo from the above thing under the conditions which reduced the Mn content and the Si content, it turns out that the above high-temperature-oxidation-proof characteristic is shown like [what has low Al content] conventional ferritic stainless steel containing high Al. And the material which can be hot-rolled without an improvement of toughness being achieved by low Mn and low Si, and generating defects, such as a crack, by them was obtained.

[0023]Example 2: The various steel shown in Table 2 was used, and the foil material of 50 micrometers of board thickness was manufactured like Example 1. A 1150 ** oxidation test was presented with each test specimen, and the time when catastrophic oxidation occurred was measured. A test result is combined with Table 2 and shown.

[Table 2]

表2： 異常酸化に与える合金成分の影響

試験	合金成分及び含有量 (重量%)											異常酸化発生	衝撃靭性	適
番号	C	Si	Mn	P	S	Cr	Al	Mo	REM	Y	その他	時間 (時)	(J／cm²)	用
1	0.011	0.10	0.14	0.026	0.0020	20.12	3.81	1.78	0.06	—	—	270	22	本発明鋼
2	0.012	0.16	0.18	0.024	0.0021	20.18	3.73	1.32	0.06	—	Ti：0.04	200	20	
3	0.012	0.07	0.11	0.023	0.0009	18.02	2.96	1.81	—	0.07	—	290	25	
4	0.013	0.08	0.14	0.023	0.0019	20.16	2.67	1.92	0.04	—	—	190	31	
5	0.009	0.11	0.07	0.024	0.0021	20.11	3.65	0.96	0.04	—	V：0.09	190	31	
6	0.012	0.09	0.10	0.025	0.0016	20.08	4.33	0.87	0.05	—	—	340	23	
7	0.014	0.10	0.17	0.024	0.0021	20.29	4.24	1.90	—	0.06	—	520	19	
8	0.012	0.35	0.32	0.026	0.0020	20.21	5.09	—	0.06	—	—	160	11	比較鋼
9	0.010	0.32	0.31	0.024	0.0021	20.11	3.06	—	0.06	—	Ti：0.05	60	38	
10	0.012	0.08	0.11	0.023	0.0009	19.10	3.11	—	0.04	—	—	75	39	
11	0.010	0.25	0.36	0.024	0.0018	20.08	3.16	3.11	0.05	—	V：0.05	310	9	
12	0.012	0.08	0.45	0.022	0.0020	20.09	0.81	1.83	—	0.05	—	40	37	
13	0.010	0.36	0.09	0.022	0.0017	20.04	5.36	3.36	0.05	—	—	—	—	

[0024]As for each test specimen of the test numbers 1-7 according to this invention,

catastrophic oxidation generating time is over 200 hours.
The high-temperature-oxidation-proof characteristic of having excelled the comparison steel 8 currently used from the former for metallic converters was shown.
The test specimen of the test numbers 1-7 showed the shock toughness which excelled more than 19 J/cm^2 as a hot-rolled hot coil. Therefore, it excelled in manufacturability, and since working capacity was good and there were few falls of the yield, the manufacturing cost was able to be made low. On the other hand, since Al content is low, catastrophic oxidation has generated the comparison steel 9, 10, and 12 within 75 hours of what has good shock toughness.
It was inferior to the high-temperature-oxidation-proof characteristic.
The comparison steel 11 which made both Al content and Mo content 3 % of the weight or more had the very low shock toughness of what has good high-temperature-oxidation-proof nature, and was difficult to manufacture. Since the comparison steel 13 contains aluminum, Si, and Mo so much, its toughness is dramatically low and cannot hot-roll it.
[0025]
[Effect of the Invention]As explained above, even if Al content is comparatively low in aluminum content ferritic stainless steel of this invention by adding Mo of a specific amount under the conditions of low Mn and low Si, the outstanding high-temperature-oxidation-proof characteristic can be given. And reduction of Mn and Si improves the toughness of ferritic stainless steel and manufacturability, and processability conjointly with the fall of Al content. Therefore, the material which fitted high-temperature-service ways, such as a metallic converter, at cheap cost is obtained.

[Translation done.]